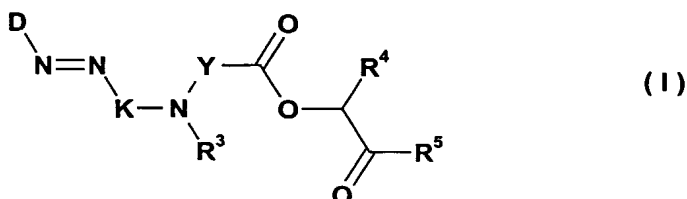


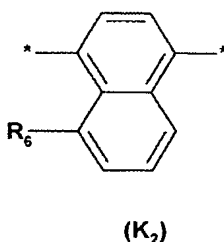
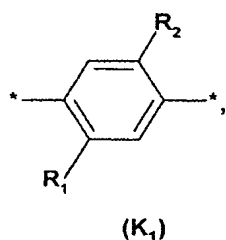
DISPERSE DYES

The invention relates to disperse dyes of the general formula (I)

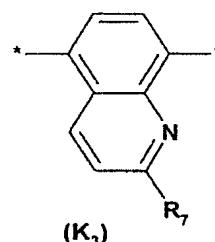


where

- D is a diazo component derived from a substituted or unsubstituted aromatic amine,
 10 K is an aromatic radical of the formula K₁, K₂ or K₃



or



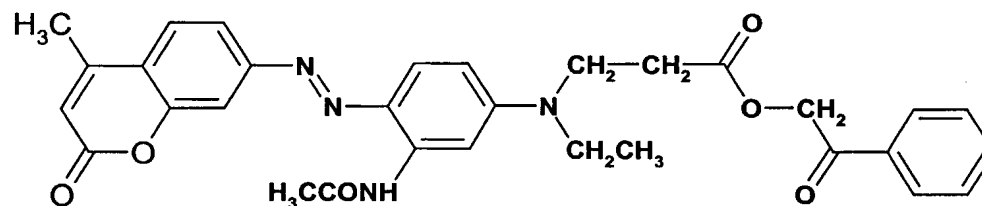
- R₁ is hydrogen, chlorine, C₁₋₂-alkyl, C₁₋₂-alkoxy, hydroxyl or acylamino,
 15 R₂ is hydrogen, C₁₋₄-alkoxy, C₁₋₂-alkoxyethoxy, chlorine, bromine or combines with R₃ to form a group of the formula -*CH(CH₃)CH₂C(CH₃)₂- (* attached to the nucleus),
 R₃ is hydrogen, C₁₋₆-alkyl, C₃₋₄-alkenyl, chloro- or bromo-C₃₋₄-alkenyl, C₃₋₄-alkynyl, phenyl-C₁₋₃-alkyl, C₁₋₄-alkoxycarbonyl-C₁₋₃-alkyl, C₃₋₄-alkenyloxycarbonyl-C₁₋₃-alkyl, C₃₋₄-alkynyloxycarbonyl-C₁₋₃-alkyl, phenoxy-C₂₋₄-alkyl, halogen-, cyano-, C₁₋₄-alkoxy-, C₁₋₄-alkylcarbonyloxy- or C₁₋₄-alkoxycarbonyloxy-substituted C₂₋₄-alkyl, or a group of the formula -CH₂-CH(R₈)CH₂-R₉,
 20 R₄ is hydrogen or C₁₋₂-alkyl,
 R₅ is phenyl which may be substituted by one or two substituents selected from the group consisting of methyl, chlorine, bromine and nitro or combines with R₄ to
 25 form a c-pentanone or c-hexanone ring,

- R_6 is hydrogen or hydroxyl,
 R_7 is hydrogen or methyl,
 R_8 is hydroxyl or C_{1-4} -alkylcarbonyloxy,
 R_9 is chlorine, C_{1-4} -alkoxy, phenoxy, allyloxy or C_{1-4} -alkylcarbonyloxy,
 5 Y is C_{1-3} -alkylene,

wherein R_3 is just hydrogen when K is a radical of the formula K_2 or K_3 .

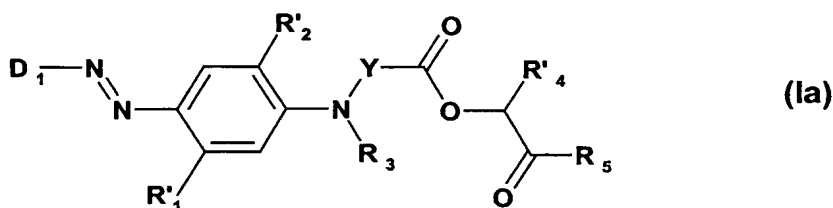
Excluded from the invention is the dye compound of the formula

10



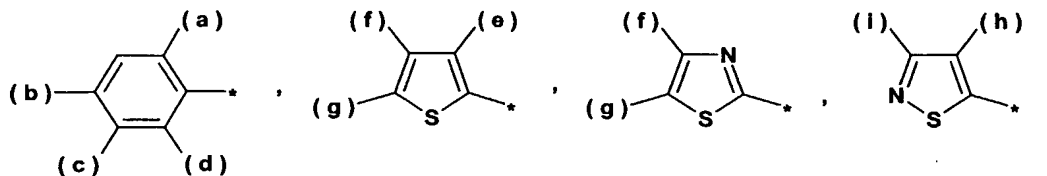
as disclosed in example 29 of WO 2004/035690 A1 .

- 15 A group of preferred dyes of the formula I conform to the general formula (Ia)

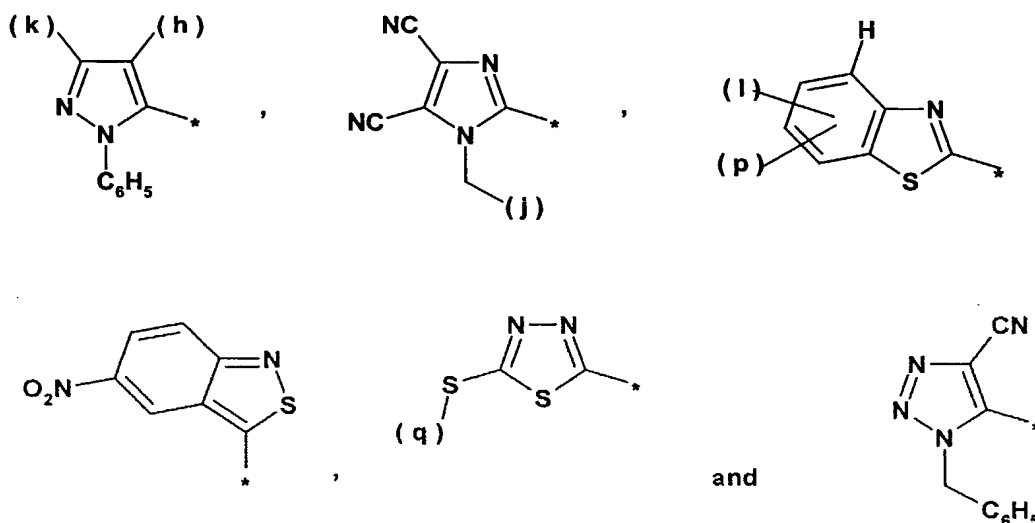


where

- 20 D_1 is 3-phenyl-1,2,4-thiadiazolyl or conforms to one of the following formulae:



3



5 where

- (a) is hydrogen, chlorine, bromine, cyano, nitro-, C₁₋₄-alkoxycarbonyl, C₁₋₃-alkylsulphonyl, preferably hydrogen, chlorine, cyano or nitro,
- (b) is chlorine, bromine, nitro, methyl, C₁₋₂-alkylsulphonyl, C₁₋₄-alkylcarbonyl, aminosulphonyl, mono- or di-C₁₋₄-alkylaminosulphonyl, phenylaminosulphonyl,
- 10 C₁₋₄-alkoxycarbonyl, benzyloxycarbonyl, tetrahydrofurfuryl-2-oxycarbonyl, C₃₋₄-alkenyloxycarbonyl, C₃₋₄-alkynyloxycarbonyl, aminocarbonyl, mono- or di-C₁₋₄-alkylaminocarbonyl, phenylaminocarbonyl or phenylazo,
- (c) is hydrogen or chlorine or else (when d is hydrogen) hydroxyl or rhodan,
- (d) is hydrogen, chlorine, bromine, hydroxyl or cyano,
- 15 (e) is nitro, C₁₋₄-alkylcarbonyl, C₁₋₄-alkoxycarbonyl, cyano, aminocarbonyl, mono- or di-C₁₋₄-alkylaminocarbonyl,
- (f) is hydrogen, chlorine, bromine, C₁₋₂-alkyl or phenyl,
- (g) is nitro, cyano, formyl, dicyanovinyl or a group of the formula -CH=CH-NO₂, -CH=C(CN)CO-OC₁₋₄-alkyl, H₅C₆-N=N- or 3- or 4-NO₂-C₆H₄-N=N-,
- 20 (h) is cyano or C₁₋₄-alkoxycarbonyl,
- (i) is C₁₋₄-alkyl or phenyl,
- (j) is -CN, -CH=CH₂ or phenyl,
- (k) is C₁₋₄-alkyl,
- (l) is hydrogen, chlorine, bromine, cyano, rhodan, nitro, C₁₋₄-alkoxycarbonyl or
- 25 di-C₁₋₄-alkylaminosulphonyl,
- (p) is hydrogen, chlorine or bromine, and
- (q) is C₁₋₄-alkyl or C₁₋₄-alkoxycarbonyl-C₁₋₄-alkyl,

wherein the phenyl nuclei of these substituents may bear one or two substituents selected from the group consisting of chlorine, bromine, methyl and C₁₋₂-alkoxy,

R'₁ is hydrogen, methyl, chlorine or acylamino,

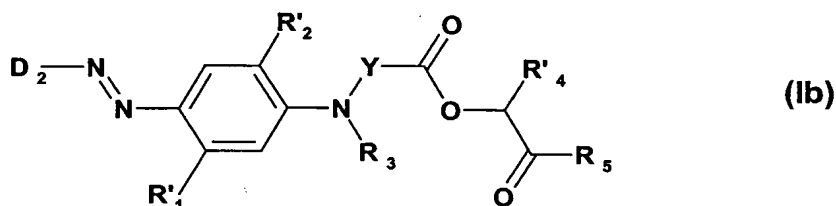
5 R'₂ is hydrogen, chlorine, C₁₋₂-alkoxy, C₁₋₂-alkoxyethoxy or combines with R₃ to form a group of the formula -CH(CH₃)CH₂C(CH₃)₂-,

R₃ and R₅ are each as defined above,

R'₄ is hydrogen or methyl, and

Y is a group of the formula -CH₂CH₂- or -CH₂CH(CH₃)-.
 10

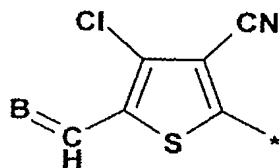
Particular preference is given to disperse dyes of the formula (Ib)



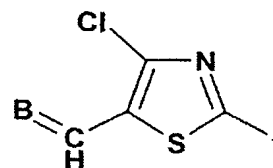
15 where

D₂ is the residue of a diazo component of the formula 2,6-dicyano-4-chloro-, 2,6-dicyano-4-bromo-, 2,6-dicyano-4-methyl-, 2,6-dicyano-4-nitrophenyl, 2,4-dinitro-6-chloro-, 2,4-dinitro-6-bromo- or 2,4-dinitro-6-cyanophenyl, 2-chloro-4-nitro-6-cyanophenyl, 2-bromo-4-nitro-6-cyanophenyl, 2,4-dinitrophenyl, 2,6-dichloro-4-nitrophenyl, 2,6-dibromo-4-nitrophenyl, 2-chloro-4-nitro-6-bromophenyl, 2-chloro-4-nitrophenyl, 2-cyano-4-nitrophenyl, 2,4-dinitro-5,6-dichlorophenyl, 2,5-dichloro-4-nitrophenyl, 4-nitro-phenyl, 4-phenylazophenyl, 4-C₁₋₄-alkoxycarbonylphenyl, 2-C₁₋₄-alkoxy-carbonyl-4-nitrophenyl, 4-benzyloxycarbonylphenyl, 4-(tetrahydrofurfuryl-2'-oxycarbonyl)phenyl, 3,5-dicyano-4-chloro-thienyl-2, 3,5-dicyano-thienyl-2, 3-cyano-5-nitro-thienyl-2, 3-acetyl-5-nitro-thienyl-2, 3,5-dinitro-thienyl-2, 3-(C₁₋₄-alkoxycarbonyl)-5-nitro-thienyl-2, 5-phenylazo-3-cyano-thienyl-2, 5-phenylazo-3-cyano-4-methyl-thienyl-2, 5-nitro-thiazolyl-2, 5-nitrobenzothiazolyl-3, 3-methyl-4-cyano-isothiazolyl-5, 3-phenyl-1,2,4-thiadiazolyl-2, 5-(C₁₋₂-alkylmercapto)-1,3,4-thiadiazolyl-2, 3-(C₁₋₂-alkoxycarbonyl-ethyl-mercapto)-1,2,4-thiadiazolyl-5, 1-cyanomethyl-4,5-dicyano-imidazolyl-2, 6-nitrobenzothiazolyl-2, 5-nitrobenzothiazolyl-2, 6-rhodanbenzothiazolyl-2, 6-chlorobenzothiazolyl-2, (5),6,(7)-dichlorobenzothiazolyl-2, or of the formula
 20
 25
 30

5



or



and B is oxygen or a group of the formula $=(\text{CN})_2$, $=\text{CH}-\text{NO}_2$, $=(\text{CN})-\text{COOC}_{1-4}\text{alkyl}$ or $=(\text{CN})-\text{COOC}_{3-4}\text{alkenyl}$

5

and the symbols R'_1 , R'_2 , R_3 , R'_4 , R_5 and Y are each as defined above.

Particular preference is further given to the disperse dyes of the formula I where

- 10 D is a diazo component selected from the group consisting of 2,4-dinitro-6-chlorophenyl, 2,4-dinitro-6-bromophenyl, 2,4-dinitro-6-cyanophenyl or 2,6-dicyano-4-nitrophenyl,
- K is a radical of the formula K_1 ,
- R_1 is C_{1-2} -alkylcarbonylamino with or without bromine, chlorine, hydroxyl or C_{1-2} -alkoxy substitution; phenylaminocarbonyl, methylsulphonylamino, methyl or
- 15 hydrogen,
- R_2 is C_{1-2} -alkoxy or hydrogen,
- R_3 is hydrogen, C_{1-4} -alkyl, cyanoethyl, C_{1-2} -alkoxyethyl or C_{3-4} -alkenyl
- R_4 is hydrogen,
- 20 R_5 is phenyl, and
- Y is a group of the formula $-\text{CH}_2\text{CH}_2-$.

Useful diazo components include all mono- to binuclear carbo- or heterocyclic organic radicals or residues of aromatic character which can bear customary disperse dye

25 substituents except in particular water-solubilizing substituents, i.e. sulphonic acid groups especially. Useful diazo components further include residues of monoazo compounds. Examples of diazo components are: preferably substituted phenyl, thienyl, thiazolyl, isothiazolyl, thiadiazolyl, pyrazolyl, imidazolyl, triazolyl, benzothiazolyl or benzoisothiazolyl radicals.

30

All the alkyl groups mentioned contain, unless otherwise stated, 1 to 8 and especially 1 to 4 carbon atoms, they can be straight-chain or branched and may be substituted, for example by halogen atoms, preferably bromine or chlorine atoms, hydroxyl, alkoxy, phenyl, phenoxy, cyano, rhodan, acyl, acyloxy or acylamino groups.

5

The Y interlink is preferably a group of the formula $-\text{CH}_2\text{CH}_2-$ or $-\text{CH}_2\text{CH}(\text{CH}_3)-$ especially $-\text{CH}_2\text{CH}_2-$.

All alkyl, alkylene and alkenyl radicals are straight chain, unless stated otherwise.

10

The process for preparing the novel dyes of the formula (I) is characterized in that a diazotized amine of the formula (II)

D-NH₂ (II)

15

is coupled with a compound of the formula (III)

H-K (III).

20

Diazotizing and coupling are carried out according to commonly known methods.

The compounds of the formulae II and III are known or are easy to prepare from known compounds by methods known to one skilled in the art.

25

The novel dyes of the formula (I) exhibit excellent exhaustion from an aqueous suspension onto textile material composed of manufactured synthetic or natural polymer hydrophobic macromolecular organic substances. They are particularly useful for dyeing or printing textile material composed of linear aromatic polyesters and also of cellulose acetate and cellulose triacetate.

30

Dyeing or printing is accomplished by processes known per se, for example those described in French patent 1 445 371.

35

The dyeings obtained have good allround fastnesses; worth emphasizing are the light fastness, the fastness to dry heat setting and coating and also the excellent wet fastnesses, after thermal stabilization (thermomigration fastness).

The formulae (I) dyes used according to the invention can be used for dyeing and printing manufactured natural polymer and especially synthetic hydrophobic fibre materials, in particular textile materials. Textile materials composed of blend fabrics comprising such manufactured natural polymer or synthetic hydrophobic fibre materials
5 are likewise dyeable or printable with the dyes of the formula (I).

Useful manufactured natural polymer hydrophobic textile materials include for example acetate filament (cellulose acetate) and cellulose triacetate.

10 Synthetic hydrophobic textile materials consist for example of linear aromatic polyesters, for example polyesters from terephthalic acid and glycols, particularly ethylene glycol, or condensation products of terephthalic acid and 1,4-bis-(hydroxymethyl)-cyclohexane; of polycarbonates, for example those formed from alpha, alpha-dimethyl-4,4'-dihydroxydiphenylmethane and phosgene, of fibres based on
15 polyvinyl chloride and especially on polyamide.

The textile material mentioned may be present at dyeing or printing in the various processing forms, for example as fibre, yarn or web, as a woven or loop-formingly knitted fabric or in the form of carpets.

20 The dyes of the formula (I) are applied to the textile materials by known dyeing processes. For example, polyester fibre materials are exhaust dyed from an aqueous dispersion in the presence of customary anionic or nonionic dispersants with or without customary carriers at temperatures between 80 and 140°C. Cellulose acetate is
25 preferably dyed at between about 65 to 85°C and cellulose triacetate at temperatures of up to 115°C.

Polyamide-based fibre materials are preferably dyed at a pH of 3 to 7 and especially 3 to 5. The dyeing is preferably carried out at a temperature of 70 to 110°C and
30 especially 80 to 105°C.

The liquor ratio depends on the apparatus, the substrate and the make-up form. However, the liquor ratio can be chosen within a wide range, for example from 4 : 1 to 100 : 1, but preferably 5 : 1 to 30 : 1.

35

The formula (I) dyes used according to the invention can be applied in the customary dyeing processes, such as for example in the exhaust process, continuous process or printing process.

- 5 The formula (I) dyes used according to the invention are also useful for dyeing from short liquors, for example in continuous dyeing processes or batch and continuous foam dyeing processes.

Preference is given to dyeing, especially dyeing by the exhaust process.

10

The dyeing liquors or print pastes, in addition to water and the dyes, may contain further additives, for example wetting agents, antifoams, levelling agents or agents to influence the properties of the textile material, for example softeners, flame retardants or soil, water and oil repellants, and also water softeners and natural or synthetic
15 thickeners, for example alginates or cellulose ethers.

The amounts in which the dyes of the formula (I) are used in the dyebaths or print pastes can vary within wide limits, depending on the desired depth of shade.

- Advantageous amounts will generally be in the range from 0.01% to 15% by weight
20 and especially 0.1% to 10% by weight, based on the weight of fibre and based on the print paste, respectively.

- The dyes of the formula (I) can likewise be used for mass coloration of polyester. The disperse dyes according to the invention can also first be processed into concentrates
25 in which a polymer which is compatible with the polymer to be coloured serves as a carrier for the disperse dyes. The carrier material should belong to the same category of polymers or be a generally high-compatible substance. This avoids adverse repercussions for the mechanical, thermal and optical properties. Such preparations contain the disperse dyes according to the invention (or generally pigments and/or
30 dyes) in highly concentrated form in a polymer-carrier adapted to the end product and which are used for mass coloration of polymers are customarily termed masterbatches. Alternatively, pellets or liquid formulations (dispersions) or simply dry blends can also be prepared for mass coloration of polymers.

- 35 The disperse dyes according to the invention are useful for pigmenting macromolecular organic materials of natural or synthetic origin, for example plastics, resins, coatings,

paints, electrophotographic toners and developers, colour filters and also inks, including printing inks.

5 The disperse dyes according to the invention are also useful as colorants in aqueous and non-aqueous ink jet inks, microemulsion inks and also in such inks which are employed in the hot melt process.

10 Ink jet inks generally contain in total 0.5% to 15% by weight and preferably 1.5% to 8% by weight (reckoned dry) of one or more of the disperse dyes according to the invention.

15 Microemulsion inks are based on organic solvents, water and if appropriate an additional hydrotropic substance (interface mediator). Microemulsion inks contain in general 0.5% to 15% by weight and preferably 1.5% to 8% by weight of one or more of the disperse dyes according to the invention, 5% to 99% by weight of water and 0.5% to 94.5% of organic solvent and/or hydrotropic compound.

20 "Solvent-based" ink jet inks contain preferably 0.5% to 15% by weight of one or more of the disperse dyes according to the invention, 85% to 99.5% by weight of organic solvent and/or hydrotropic compounds.

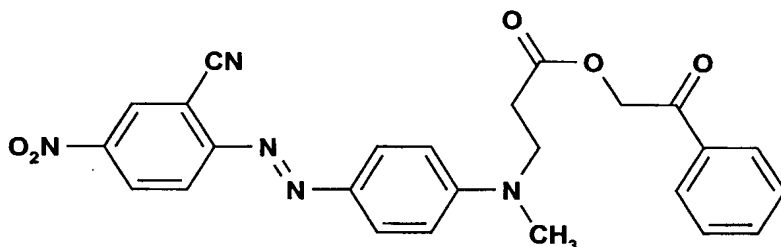
25 Hot-melt inks are usually based on waxes, fatty acids, fatty alcohols or sulphonamides which are solid at room temperature and become liquid on heating, the preferred melting range being situated between about 60°C and about 140°C. Hot-melt ink jet inks consist essentially for example of 20% to 90% by weight of wax and 1% to 10% by weight of one or more of the disperse dyes according to the invention. There may further be included 0% to 20% by weight of an additional polymer (as "dye-dissolver"), 0% to 5% by weight of dispersing assistant, 0% to 20% by weight of viscosity modifier, 0% to 20% by weight of plasticizer, 0% to 10% by weight of tack additive, 0% to 10% by weight of transparency stabilizer (prevents crystallization of waxes, for example) and also 0% to 2% by weight of antioxidant.

35 Parts and percentages in the examples which follow are by weight. The temperatures are indicated in degrees Celsius.

EXAMPLE 1

16.3 parts of 2-cyano-4-nitroaniline are suspended in 100 parts of cold sulphuric acid 93% and admixed with 32 parts of nitrosylsulphuric acid (40%) at 0-5°C in the course of 30 minutes. This is followed by 3-4 hours of stirring at 0-5°C, and then the resulting
5 diazonium salt solution is poured continuously with stirring into a mixture of 29.7 parts of phenylcarbonylmethyl 3-(N-methyl-N-phenylamino)-propionate, 100 parts of glacial acetic acid, 2 parts of sulphamic acid, 200 parts of water and 300 parts of ice. The precipitated dye is filtered off, washed acid free with water and dried at 60°C under reduced pressure. The dye obtained conforms to the formula

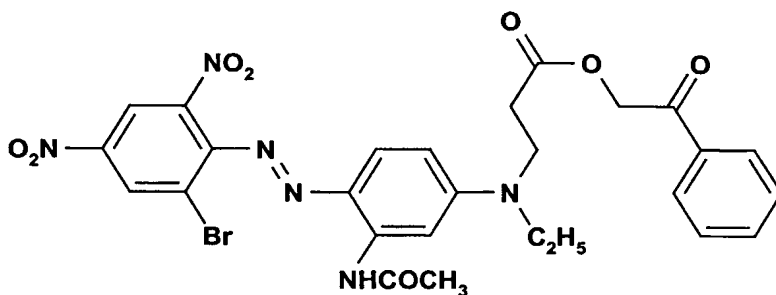
10



It dyes polyester fibre material in ruby shades having excellent fastnesses, especially very good wet fastnesses after thermal stabilization, and is very useful, alone or in
15 mixtures, for state of the art rapid-dyeing processes such as for example the ®Foron RD process. $\lambda_{\text{max}} = 530 \text{ nm}$ (DMF)

EXAMPLE 2

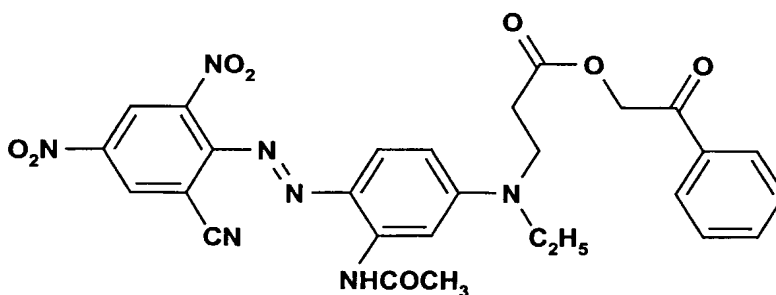
26.2 parts of 2-bromo-4,6-dinitroaniline are suspended in 150 parts of sulphuric acid 93% at 15-20°C and admixed with 32 parts of nitrosylsulphuric acid 40% in the course of 30 minutes. This is followed by 2-3 hours of stirring, and the diazonium salt solution is poured continuously with stirring into a mixture of 36.8 parts of phenylcarbonylmethyl 3-(N-ethyl-N-(3'-acetylamino-phenylamino))-propionate, 100 parts of glacial acetic acid,
25 2 parts of sulphamic acid, 100 parts of water and 200 parts of ice. The precipitated dye is filtered off, washed acid free with water and dried at 60°C under reduced pressure. The dye obtained conforms to the formula



and dyes polyester fibre material in violet shades having excellent fastnesses. The dye, which has $\lambda_{\max} = 559$ (DMF), is very useful, alone or in navy or black mixtures, for state of the art rapid-dyeing processes such as for example the [®]Foron RD process.

EXAMPLE 3

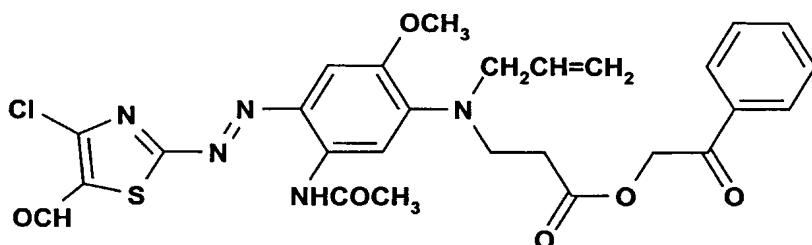
64.1 parts of 2-bromo-4,6-dinitroaniline-1-azo dye (preparation according to Example 2), 1 part of potassium iodide are suspended in 200 parts of dimethyl sulfoxide at 60°C, admixed with 9.8 parts of copper(I) cyanide and stirred for 2-3 hours. The reaction product is filtered off at about 50°C, washed with 50 parts of 1:1 DMSO / water in portions and dried at 60°C under reduced pressure. The dye obtained conforms to the formula



and dyes polyester fibre material in blue shades having excellent fastnesses, especially having excellent wet fastnesses. The dye, which has $\lambda_{\max} = 604$ (DMF), is, alone or in mixtures, very useful for state of the art rapid-dyeing processes such as for example the [®]Foron RD process.

EXAMPLE 4

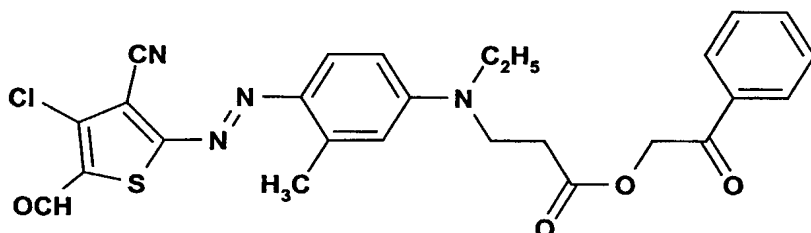
16.3 parts of 2-amino-4-chloro-5-formylthiazole are dissolved in 100 parts of sulphuric acid 93% and admixed with 32 parts of nitrosylsulphuric acid 40% at 0 to 5°C in the course of 30 minutes. This is followed by 3 hours of stirring in an icebath, and the
5 diazonium salt solution is poured continuously into a mixture of 41.0 parts of phenylcarbonylmethyl 3-[N-allyl-N-(5'-acetylamino-2'-methoxy-phenylamino)]-propionate, 100 parts of glacial acetic acid, 2 parts of sulphamic acid and 300 parts of ice/water. The precipitated dye is filtered off, washed acid free with water and dried at 60°C under reduced pressure. The dye obtained, which has $\lambda_{\max} = 625$ (DMF),
10 conforms to the formula



and dyes polyester materials in greenish navy shades and is useful as individual dye or
15 in navy and black mixtures for the ®Foron RD rapid-dyeing process, with very good fastnesses.

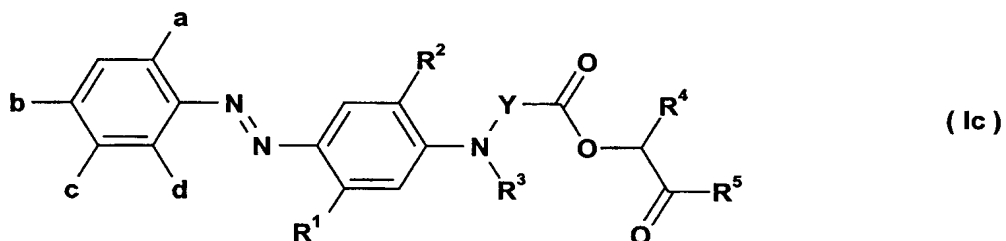
EXAMPLE 5

18.6 parts of 2-amino-4-chloro-3-cyano-5-formylthiophene are dissolved in 200 parts of cold sulphuric acid 85%. 32 parts of nitrosylsulphuric acid 40% are added dropwise with stirring at 0 to 5°C in the course of 30 minutes. This is followed by 3 hours of stirring in an icebath, and the diazonium salt solution is poured continuously into a mixture of 32.5 parts of phenylcarbonylmethyl 3-[N-ethyl-N-(3'-methylphenylamino)]-
20 propionate, 50 parts of 5% sulphuric acid, 2 parts of sulphamic acid and 300 parts of ice. The precipitated dye is filtered off, washed acid free with water and dried at 60°C under reduced pressure. The dye obtained having $\lambda_{\max} = 610$ (DMF), conforms to the formula



and dyes polyester materials in brilliant reddish blue shades having good fastnesses.

- 5 **Table 1** below indicates further dyes of the general formula (Ic); they are prepared similarly to Examples 1 to 5.



- 10 and **Table 2** subsequently indicates further dyes of the general formula (Id); they are prepared similarly to Examples 1 to 5.

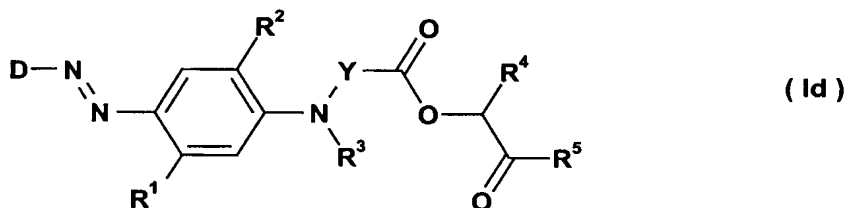


TABLE 1 (dyes of the general formula (Ic))

Ex.	(a)	(b)	(c)	(d)	Y	R ¹	R ²	R ³	R ⁴	R ⁵	λ_{\max} (DMF)
6	NO ₂	NO ₂	H	Br	-C ₂ H ₄ -	NHCOCH ₃	H	n-C ₃ H ₇	H	C ₆ H ₅	560
7	NO ₂	NO ₂	H	CN	-C ₂ H ₄ -	NHCOCH ₃	H	n-C ₃ H ₇	H	C ₆ H ₅	611
8	NO ₂	NO ₂	H	CN	-C ₂ H ₄ -	NHCOC ₂ H ₅	H	C ₂ H ₅	H	C ₆ H ₅	612
9	NO ₂	NO ₂	H	CN	-C ₂ H ₄ -	NHCOCH ₃	H	CH ₂ CH=CH ₂	H	C ₆ H ₅	608
10	NO ₂	NO ₂	H	CN	-C ₂ H ₄ -	NHCOCH ₃	H	C ₂ H ₄ OCH ₃	H	C ₆ H ₅	609
11	NO ₂	NO ₂	H	CN	-C ₂ H ₄ -	NHCOCH ₃	H	CH ₂ CHOHCH ₂ Cl	CH ₃	C ₆ H ₅	608
12	NO ₂	NO ₂	H	CN	-C ₂ H ₄ -	NHCOCH ₂ Cl	H	C ₂ H ₅	H	C ₆ H ₅	605
13	NO ₂	NO ₂	H	CN	-C ₂ H ₄ -	NHCOCH ₂ CH ₂ Cl	H	C ₂ H ₅	H	C ₆ H ₅	607
14	CN	NO ₂	H	CN	-C ₂ H ₄ -	NHCOCH ₃	H	n-C ₄ H ₉	H	CH ₃	615
15	CN	NO ₂	H	CN	-C ₂ H ₄ -	NHCOCH ₃	H	n-C ₃ H ₇	H	C ₂ H ₅	614
16	CN	NO ₂	H	CN	-C ₂ H ₄ -	NHCOCH ₃	H	C ₂ H ₅	H	C ₆ H ₅	613
17	NO ₂	NO ₂	H	CN	-C ₂ H ₄ -	NHCOCH ₃	H	CH ₃	H	C ₆ H ₅	610
18	NO ₂	NO ₂	H	CN	-C ₂ H ₄ -	NHCOCH ₃	H	CH ₂ C(CH ₃)H=CH ₂	H	C ₆ H ₅	612
19	NO ₂	NO ₂	H	Cl	-C ₂ H ₄ -	NHCOCH ₂ OCH ₃	OC ₂ H ₅	H	H	C ₆ H ₅	596
20	NO ₂	NO ₂	H	Cl	-C ₂ H ₄ -	NHCOCH ₂ Cl	OCH ₃	H	H	C ₆ H ₅	594
21	NO ₂	NO ₂	H	Cl	-C ₂ H ₄ -	NHCOCH=CH ₂	OCH ₃	-C ₆ H ₁₃	H	C ₆ H ₅	608
22	NO ₂	NO ₂	H	Cl	-C ₂ H ₄ -	NHCHO	OCH ₃	CH ₂ C ₆ H ₅	H	C ₆ H ₅	602
23	NO ₂	NO ₂	H	Cl	-CH ₂ -	NHCOCH ₃	OCH ₃	H	H	C ₆ H ₅	596
24	NO ₂	NO ₂	H	Br	-C ₂ H ₄ -	NHCOCH ₃	OCH ₃	H	H	C ₆ H ₅	597
25	NO ₂	NO ₂	H	Br	-C ₂ H ₄ -	NHCOCH ₃	OCH ₃	C ₂ H ₄ OCOCH ₃	H	C ₆ H ₅	591

26	NO ₂	NO ₂	H	J	-C ₂ H ₄ -	NHCOCH ₃	OCH ₃	C ₂ H ₄ OCH ₃	H	C ₆ H ₅	594
27	NO ₂	NO ₂	H	CN	-C ₂ H ₄ -	NHCOCH ₃	H	CH ₂ CH ₂ CH ₂ Cl	H	C ₆ H ₅	609
28	NO ₂	NO ₂	H	CN	-CHCH ₃ CH ₂ -	NHCOCH ₃	H	C ₂ H ₄ OC ₂ H ₄ OCH ₃	H	C ₆ H ₅	608
29	NO ₂	NO ₂	H	CN	-C ₂ H ₄ -	NHCOCH ₃	H	CH ₂ CH ₂ CH ₂ CH ₂ OCOCH ₃	H	C ₆ H ₅	612
30	NO ₂	NO ₂	H	CN	-C ₂ H ₄ -	NHCOCH ₃	H	CH ₂ CH(OCOCH ₃)CH ₃	H	C ₆ H ₅	601
31	CN	NO ₂	H	CN	-C ₂ H ₄ -	NHCOCH ₃	H	CH ₂ C ₆ H ₅	H	C ₆ H ₅	597
32	CN	NO ₂	H	CN	-C ₂ H ₄ -	NHCOC ₂ H ₅	H	CH ₂ C ₆ H ₅	H	C ₆ H ₅	598
33	CN	NO ₂	H	CN	-CH ₂ -	NHCOCH ₃	OCH ₃	CH ₂ C ₆ H ₅	H	C ₆ H ₅	635
34	NO ₂	NO ₂	H	Br	-C ₂ H ₄ -	NHCOCH ₃	OCH ₃	CH ₂ C ₆ H ₅	H	C ₆ H ₅	593
35	NO ₂	NO ₂	H	Cl	-C ₂ H ₄ -	NHCOCH ₃	OCH ₃	CH ₂ C ₆ H ₅	CH ₃	C ₆ H ₅	594
36	NO ₂	NO ₂	H	Cl	-(CH ₂) ₃ -	NHCOOCH ₃	OCH ₃	C ₂ H ₄ OCOCH ₃	H	C ₆ H ₅	591
37	CN	NO ₂	H	Br	-C ₂ H ₄ -	NHCOCH ₃	H	C ₂ H ₅	H	*-(CH ₂) ₃ -	584
38	CN	NO ₂	H	Br	-C ₂ H ₄ -	NHCOC ₂ H ₅	H	n-C ₃ H ₇	H	C ₆ H ₅	585
39	CN	NO ₂	H	Cl	-C ₂ H ₄ -	NHCOCH ₃	H	C ₂ H ₅	H	C ₆ H ₅	584
40	CN	NO ₂	H	H	-C ₂ H ₄ -	NHCOCH ₃	H	C ₂ H ₅	H	C ₆ H ₅	554
41	CN	NO ₂	H	H	-CHCH ₃ CH ₂ -	NHCOCH ₃	H	C ₂ H ₅	H	C ₆ H ₅	555
42	CN	NO ₂	H	H	-C ₂ H ₄ -	H	H	CH ₂ CH=CH ₂	H	C ₆ H ₅	532
43	CN	NO ₂	H	H	-C ₂ H ₄ -	H	H	CH ₂ C ₆ H ₅	H	C ₆ H ₅	530
44	CN	NO ₂	H	H	-C ₂ H ₄ -	H	H	C ₂ H ₄ OC ₆ H ₅	H	C ₆ H ₅	534
45	Cl	NO ₂	H	H	-C ₂ H ₄ -	NHCOCH ₃	H	CH ₂ CH=CH ₂	H	C ₆ H ₅	527
46	Cl	NO ₂	H	H	-C ₂ H ₄ -	NHCOCH ₃	H	CH ₂ COOC ₂ H ₅	H	C ₆ H ₅	517
47	COOCH ₃	NO ₂	H	H	-C ₂ H ₄ -	NHCOCH ₃	H	CH ₂ C ₆ H ₅	H	C ₆ H ₅	528
48	Cl	NO ₂	H	H	-C ₂ H ₄ -	NHCOCH ₃	H	CH ₂ C ₆ H ₅	H	C ₆ H ₅	525

49	Cl	SO ₂ CH ₃	H	H	-C ₂ H ₄ -	NHCOCH ₃	H	C ₂ H ₅	H	C ₆ H ₅	499
50	Cl	NO ₂	H	H	-C ₂ H ₄ -	NHCOCH ₃	Cl	H	H	C ₆ H ₅	505
51	OH	NO ₂	H	H	-C ₂ H ₄ -	NHCOCH ₂ OCH ₃	H	CH ₂ CH=CH ₂	H	C ₆ H ₅	520
52	OH	NO ₂	H	H	-C ₂ H ₄ -	NHCOCH ₃	H	CH ₂ C ₆ H ₅	H	C ₆ H ₅	516
53	OH	NO ₂	H	H	-C ₂ H ₄ -	H	H	C ₂ H ₅	H	C ₆ H ₅	518
54	CN	Br	H	CN	-C ₂ H ₄ -	OH	H	C ₂ H ₄ OCOCH ₂ COC ₆ H ₅	H	C ₆ H ₅	510
55	CN	CH ₃	H	CN	-C ₂ H ₄ -	NHCOCH ₃	H	CH ₂ C ₆ H ₅	H	C ₆ H ₅	526
56	H	NO ₂	H	H	-C ₂ H ₄ -	H	Cl	H	H	C ₆ H ₅	450
57	H	NO ₂	H	H	-C ₂ H ₄ -	NHCOCH ₃	H	C ₂ H ₅	H	*-(CH ₂) ₄ -	514
58	H	NO ₂	H	H	-C ₂ H ₄ -	NHCOCH ₃	H	CH ₂ C ₆ H ₅	H	C ₆ H ₅	507
59	NO ₂	NO ₂	SCN	H	-C ₂ H ₄ -	CH ₃	OCH ₃	H	H	C ₆ H ₅	601
60	NO ₂	NO ₂	SCN	H	-C ₂ H ₄ -	NHCOCH ₃	OCH ₃	H	H	C ₆ H ₅	621

TABLE 2 (dyes of the general formula (Id))

Ex.	D	Y	R ¹	R ²	R ³	R ⁴	R ⁵	λ_{\max} (DMF)
61	4-Chloro-5-formylthiazolyl-2	-C ₂ H ₄ -	H	H	C ₂ H ₅	H	C ₆ H ₅	563
62	4-Chloro-5-formylthiazolyl-2	-C ₂ H ₄ -	CH ₃	H	C ₂ H ₅	H	C ₆ H ₅	586
63	4-Chloro-5-formylthiazolyl-2	-C ₂ H ₄ -	CH ₃	OCH ₃	CH ₂ CH=CH ₂	H	C ₆ H ₅	609
64	4-Chloro-5-formylthiazolyl-2	-C ₂ H ₄ -	NHCOCH ₃	OCH ₃	CH ₂ C ₆ H ₅	H	C ₆ H ₅	622
65	4-Chloro-5-formylthiazolyl-2	-C ₂ H ₄ -	NHCOCH ₃	OCH ₃	H	H	C ₆ H ₅	608
71	5-Nitro-thiazolyl-2	-C ₂ H ₄ -	H	H	C ₂ H ₅	H	C ₆ H ₅	587
72	5-Nitro-thiazolyl-2	-C ₂ H ₄ -	CH ₃	H	C ₂ H ₅	H	C ₆ H ₅	606
73	5-Nitro-thiazolyl-2	-C ₂ H ₄ -	NHCOCH ₃	OCH ₃	H	H	C ₆ H ₅	630
66	4-Chloro-3-cyano-5-formylthienyl-2	-C ₂ H ₄ -	H	H	C ₂ H ₅	H	C ₆ H ₅	593
67	4-Chloro-3-cyano-5-formylthienyl-2	-C ₂ H ₄ -	CH ₃	H	C ₂ H ₅	H	C ₆ H ₅	608
68	4-Chloro-3-cyano-5-formylthienyl-2	-C ₂ H ₄ -	NHCOCH ₃	H	C ₂ H ₅	CH ₃	C ₆ H ₅	606
69	4-Chloro-3-cyano-5-formylthienyl-2	-C ₂ H ₄ -	NHCOCH ₃	OCH ₃	H	H	C ₆ H ₅	630
70	4-Chloro-3-cyano-5-formylthienyl-2	-C ₂ H ₄ -	NHCOCH ₃	OCH ₃	C ₂ H ₅	H	C ₆ H ₅	652
71	3,5-Dinitro-thienyl-2	-C ₂ H ₄ -	NHCOCH ₃	H	C ₂ H ₅	H	C ₆ H ₅	633
72	3,5-Dinitro-thienyl-2	-C ₂ H ₄ -	CH ₃	H	C ₂ H ₅	H	C ₆ H ₅	637
73	3,5-Dinitro-thienyl-2	-C ₂ H ₄ -	H	H	C ₂ H ₅	H	C ₆ H ₅	625
74	4-Cyano-3-methyl-isothiazolyl-5	-C ₂ H ₄ -	H	H	C ₂ H ₅	H	C ₆ H ₅	543
75	4-Cyano-3-methyl-isothiazolyl-5	-C ₂ H ₄ -	NHCOCH ₃	H	CH ₂ CH=CHCl	H	C ₆ H ₅	545
76	5-Ethylmercapto-1,3,4-thiadiazolyl-2	-C ₂ H ₄ -	NHCOCH ₃	H	C ₂ H ₅	H	C ₆ H ₅	520
77	5-Ethylmercapto-1,3,4-thiadiazolyl-2	-C ₂ H ₄ -	CH ₃	H	C ₂ H ₅	H	C ₆ H ₅	518

78	5-Ethylmercapto-1,3,4-thiadiazolyl-2	-C ₂ H ₄ -	H	H	H	C ₂ H ₅	H	C ₆ H ₅	513
79	(5),6-(7)-Dichlorobenzothiazolyl-2	-C ₂ H ₄ -	H	H	H	C ₂ H ₅	H	C ₆ H ₅	535
80	(5),6-(7)-Dichlorobenzothiazolyl-2	-C ₂ H ₄ -	CH ₃	H	H	CH ₂ CH=CH ₂	H	C ₆ H ₅	537
81	(5),6-(7)-Dichlorobenzothiazolyl-2	-C ₂ H ₄ -	NHCOCH ₃	H	H	C ₂ H ₄ CN	H	C ₆ H ₅	530
82	6-Nitro-benzothiazolyl-2	-C ₂ H ₄ -	H	H	H	C ₂ H ₅	H	C ₆ H ₅	533
83	6-Methylsulphonyl-benzothiazolyl-2	-C ₂ H ₄ -	H	H	H	C ₂ H ₅	H	C ₆ H ₅	529
84	5-Nitro-2,1-benzisothiazolyl-3	-C ₂ H ₄ -	H	H	H	C ₂ H ₅	H	C ₆ H ₅	603
85	1-Cyanomethyl-4,5-dicyano-imidazolyl-2	-C ₂ H ₄ -	CH ₃	H	H	C ₂ H ₅	H	C ₆ H ₅	525
86	3-Cyano-5-phenylazo-thienyl-2	-C ₂ H ₄ -	H	H	H	C ₂ H ₅	H	C ₆ H ₅	615
87	4-Cyano-3-methyl-1-phenylpyrazolyl-5	-C ₂ H ₄ -	NHCOCH ₃	H	H	CH ₂ CH=CHCl	H	C ₆ H ₅	528
88	4-Cyano-3-methyl-1-phenylpyrazolyl-5	-C ₂ H ₄ -	NHCOCH ₃	H	H	CH ₂ CH=CH ₂	H	C ₆ H ₅	533
89	4-Cyano-1-benzyl-1,2,3-triazolyl-5	-C ₂ H ₄ -	NHCOCH ₃	H	H	C ₂ H ₅	H	C ₆ H ₅	536
90	4-Cyano-1-benzyl-1,2,3-triazolyl-5	-C ₂ H ₄ -	NHCOC ₂ H ₅	H	H	CH ₂ CH=CHCl	H	C ₆ H ₅	529